DUAL BED CATALYTIC REACTOR SYSTEM FOR DIRECT CONVERSION OF METHANE TO LIQUID HYDROCARBONS

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Faculty of Chemical and Natural Resources Engineering
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ABSTRACT

The feasibility of upgrading natural gas that primarily consists of methane to valuable chemicals, especially liquid fuel has been investigated for years. However, the high cost and inefficient processes have hampered the widespread exploitation of natural gas. Accordingly, a system comprising of a dual-bed catalytic has been investigated in this study to overcome the limitations and permit the direct conversion of methane to liquid hydrocarbons. In this dual-bed system, methane is converted in the first stage to Oxidative Coupling of Methane (OCM) products over La/MgO and the second bed comprises of H-ZSM-5 that has been tested as an oligomerization function to convert the OCM products to liquid hydrocarbons. The influence of SiO$_2$/Al$_2$O$_3$ ratio of H-ZSM-5, temperature and CH$_4$/O$_2$ ratio on the process has been studied. The results implied that the Bronsted acid sites of H-ZSM-5 were the active centers responsible for the oligomerization of primary ethylene products. Oxygen was absolutely necessary for the formation of the methyl radicals from methane, but it should be provided at a controllable manner in order to avoid undesired oxidation. The partial destruction and dealumination of H-ZSM-5 at higher temperature had caused the deactivation of the H-ZSM-5 catalyst for the oligomerization reaction. Investigation on the catalytic activity of various metals loaded H-ZSM-5 showed that incorporating nickel into H-ZSM-5 significantly enhances the yield of liquid hydrocarbons. The central composite design (CCD) coupled with response surface methodology (RSM) was successfully applied to map the response and to obtain the optimal reaction design. The results indicated that the optimum C$_{5+}$ yield of 8.91% was attained at reaction temperature = 742 °C, CH$_4$/O$_2$ ratio = 9.7 and Ni loading = 0.67 wt%. This exploration suggests that the concept of this dual-bed catalytic system is an interesting candidate for application in methane utilization to produce liquid hydrocarbons.
ABSTRAK

Keupayaan untuk mempertingkatkan gas asli yang mempunyai metana sebagai komponen utama kepada bahan kimia yang bernilai terutamanya ceair bahanapi telah diuji beberapa tahun yang lalu. Namun demikian, kos pengendalian yang tinggi dan ketidakcekapan proses telah menghadkan penguasaan meluas gas asli. Sejajar dengan itu, sistem yang mengandungi dua lapisan mangkin telah dicadangkan dalam penyelidikan ini untuk mengatasi masalah tersebut dan membolehkan penukaran terus metana kepada ceair hidrokarbon. Dalam sistem dua lapisan mangkin ini, metana ditukarkan kepada produk pengoksidaan berpasangan metana (OCM) pada peringkat pertama dan seterusnya lapisan kedua yang mengandungi H-ZSM-5 telah diuji untuk berperanan dalam tindak balas pengoligomeran untuk menukarkan produk OCM kepada ceair hidrokarbon. Pengaruh nisbah SiO₂/Al₂O₃ pada H-ZSM-5, suhu dan nisbah CH₄/O₂ ke atas proses telah dikaji. Keputusan eksperimen membuktikan bahawa asid Bronsted pada H-ZSM-5 bertindak sebagai pusat yang aktif yang berfungsi kepada tindak balas oligomerasi etena. Oksigen sangat diperlukan untuk pembentukan radikal metil daripada metana tetapi ia perlu dibekalkan pada tahap yang sesuai untuk mengelakkan pengoksidaan yang tidak diingini. Suhu tindak balas yang tinggi akan mengakibatkan kemusnahan separa dan dealuminiasi HZSM-5 yang mengurangkan keaktifan mangkin untuk tidak balas oligomerasi. Kajian ke atas aktiviti mangkin H-ZSM-5 yang mengandungi logam sebagai fungsi tambahan kepada fungsi asid menunjukkan bahawa penambahan nikel pada H-ZSM-5 jelas meningkatkan kepemilihan ceair hidrokarbon. Rekabentuk Central composite design (CCD) bergandingan dengan response surface methodology (RSM) telah digunakan dengan jayanya untuk melakarkan respon dan untuk mendapatkan rekabentuk optimum tindak balas. Keputusan menunjukkan bahawa nilai optimum kepemilihan C₅ ialah 8.91% yang dicapai pada suhu= 742 °C, nisbah CH₄/O₂=9.7 dan muatan nikel=0.67%berat. Kajian ini mencadangkan bahawa konsep yang mempunyai dua lapisan mangkin adalah satu rekabentuk yang menarik untuk digunakan dalam penukaran metana kepada ceair hidrokarbon.
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A1 Gas Chromatogram of gas standard supplied by Scott Specialty Gases

A2 Gas Chromatogram of PIONA standard
LIST OF SYMBOLS

\( a_{iC} \) - The number of atoms of the carbon presents in each molecule of the chemical species \( i \)

\( \text{Å} \) - Angstrom

\( ^0\text{C} \) - Degree Celsius

\( F \) - The ratio of mean squares due to regression to mean squares due to residual

\( F_i \) - Gas species \( i \) flowrate

\( k \) - Number of independent variables

\( K \) - Kelvin degree

\( n_0 \) - The number of experiments repeated at the center point

\( p \) - The number of terms in the fitted model

\( R^2 \) - The determinant of coefficient

\( w \) - The number of water molecules per unit cell

\( x_1 \) - The coded forms of input variables for operating temperature

\( x_2 \) - The coded forms of input variables for \( \text{CH}_4/\text{O}_2 \) ratio

\( x_3 \) - The coded forms of input variables for amount of nickel loading

\( X_i, X_j \) - The independent variables

\( Y \) - Experimental values of yield \( C_{5+} \)

\( y \) - Mol fraction

\( ¥ \) - The predicted yield of \( C_{5+} \)

\( \alpha \) - Star point value

\( \beta_1, \beta_2, \beta_3 \) - The linear terms

\( \beta_{11}, \beta_{22}, \beta_{33} \) - The squared terms

\( \beta_{12}, \beta_{13}, \beta_{23} \) - The interaction terms

\( \beta_o \) - The offset term
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<td>Advanced Gas Conversion for the 21st Century</td>
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<td>ANOVA</td>
<td>Analysis of variance</td>
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<td>BET</td>
<td>Brunauer-Emmett-Teller's surface area model</td>
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<tr>
<td>CCD</td>
<td>Central composite design</td>
</tr>
<tr>
<td>CNG</td>
<td>Compressed natural gas</td>
</tr>
<tr>
<td>DOE</td>
<td>Design of experiments</td>
</tr>
<tr>
<td>ESR</td>
<td>Epsilon Serializability Resonance</td>
</tr>
<tr>
<td>FCC</td>
<td>Fluid catalytic cracking</td>
</tr>
<tr>
<td>FID</td>
<td>Flame Ionization Detector</td>
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<td>GC</td>
<td>Gas chromatography</td>
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<td>GTL</td>
<td>Gas to Liquids technologies</td>
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<td>HT</td>
<td>Hydrogen transfer</td>
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<td>I.D.</td>
<td>Internal diameter</td>
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<td>LNG</td>
<td>Liquefied natural gas</td>
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<td>M</td>
<td>Metal</td>
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<td>MFI</td>
<td>Mobil Five Topology</td>
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<td>MTG</td>
<td>Methanol to gasoline</td>
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<td>NA</td>
<td>Nitrogen adsorption</td>
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<td>NGV</td>
<td>Natural gas vehicles</td>
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<td>NMR</td>
<td>Nuclear Magnetic Resonance</td>
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<td>NNN</td>
<td>Nearest neighbour positions</td>
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<td>OCM</td>
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<td>ODH</td>
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<tr>
<td>NODH</td>
<td>Non-Oxidative Dehydrogenation</td>
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<td>PIONA</td>
<td>Paraffins, Iso-paraffins, Olefins, Naphtha, and Aromatics</td>
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<td>REM</td>
<td>Rare-earth-metal</td>
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<td>RON</td>
<td>Research Octane Number</td>
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<tr>
<td>Acronym</td>
<td>Description</td>
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<td>RSM</td>
<td>Response surface methodology</td>
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<tr>
<td>S.S</td>
<td>Sum of square</td>
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<tr>
<td>SBU</td>
<td>Smallest number of TO$_4$ units</td>
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<td>SHOP</td>
<td>Shell higher olefin process</td>
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<td>SMDS</td>
<td>Shell Middle Distillate Synthesis</td>
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<td>Squares of the error</td>
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<td>Squares due to regression</td>
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<td>SST</td>
<td>Sum of squares</td>
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<td>Syngas</td>
<td>Synthesis gas</td>
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<td>TCD</td>
<td>Thermal conductivity detector</td>
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<td>TPD</td>
<td>Temperature programmed desorption</td>
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<td>TPR</td>
<td>Temperature programmed reduction</td>
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<td>XRD</td>
<td>X-ray diffraction</td>
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CHAPTER 1

INTRODUCTION

1.1 General Introduction

Natural gas may become more important both as an energy source and as the source of organic chemical feedstock in the 21st century (Javanmardi et al., 2005). In 2001, natural gas accounted for a 24% share of the world’s primary energy consumption (Aguiar et al., 2005). In addition, economically recoverable natural gas reserves have risen continuously over the last decades. However, the world’s natural gas reserves are located in only a few countries. The geographical distribution of natural gas is given in Figure 1.1. The largest reserves are located in the countries of the former Soviet Union and the Middle East. Future demands will be met by volumes from reserves located at even greater distances, and the investment associated with gas procurement is therefore expected to rise. Furthermore, the decline in oil production, which is forecast to occur from 2010-2020 onwards, will result in an increasing role for other fuels, most of which will be significantly more expensive (Ashman and Mullinger, 2005). Therefore, the evolution of the known natural gas reserves worldwide indicates a dramatic increase and this trend is expected to continue, which will, in addition to the price development with respect to the crude oil based upgrading-most likely generate a gradual shift towards the application of natural gas as a feedstock for the production of fuels and petrochemicals (Siddiq, 2002). This situation has forced an enhanced global interest in processes which can convert natural gas into liquids and higher added value products.
As the concerns about global warming have increased, there is more

Figure 1.1 Geographical distribution of proven natural gas (The BP Statistical Review of World Energy 2004)

On the other hand, natural gas, which is basically methane, is a colourless, odourless fossil fuel that is already widely used in homes and industry, and will be used to a greater extent in the future. It is fairly inexpensive, clean-burning, and abundant, and in recent years, it has made headlines as a solution to many environmental and economic concerns facing this country. Because it has received so much positive attention, people are now looking at ways to increase our ability to recover and utilize this resource. Although it does have some drawbacks compared to other fuels, mainly issues dealing with its volume, it promises to be an increasingly important energy source in years to come.

Natural gas has shown to be a viable substitute for other fossil fuels, namely oil and coal, as concerns over the supply of these other nonrenewable fuels grow. Natural gas is also nonrenewable; however, we have large, untouched deposits in Malaysia that, if developed, will make the sale of natural gas easier in a recognized commodities market. Also, natural gas burns cleaner and produces less pollutant than other fossil fuels. It produces 45% less CO$_2$ than coal for a comparable amount of energy, and also emits considerably less nitrogen oxide and sulphuric acid
This is a good thing, because carbon dioxide has been blamed to be the cause of the ‘greenhouse effect’.

Figure 1.2  World Primary Energy Demand (Birol and Argiri, 1999)

Projections of world energy demand by fuel are illustrated in Figure 1.2. Oil continues to dominate world energy consumption. However, recent studies, based on the current energy consumption growth, have shown that the world petroleum reserve will be depleted within the next century (Lunsford, 2000). Thus, for the survival of the world, research on alternative feedstock utilization has become one of the prime technologies of the twenty-first century and natural gas seems very promising at this stage. It burns with less emissions than gasoline, and has a higher fuel efficiency (a higher percentage of the energy in the fuel can be used). However, one concern with using natural gas is the volume of the gas, since it is much greater than that of liquid fuels. Even using CNG, (compressed natural gas), the fuel tanks of NGV’s (natural gas vehicles) must be quite large, and even then, fuel range is not as
much as if it had gasoline. On larger vehicles, such as buses, LNG (liquid natural gas) can be used. LNG is natural gas that is cooled to –166 degrees Fahrenheit, so that it condenses to a liquid (Kaneko et al., 2004). Thus, it is much more dense than CNG, although still not as energy dense as gasoline or diesel. However, in order to use LNG, the vehicle must be equipped with a large cryogenic cooling system to keep the natural gas as a liquid, so LNG is not really feasible for smaller vehicles like cars.

Because the attention on natural gas as an alternative to oil or coal is relatively new, researchers are now working on ways to increase the production, processing, and distributing abilities of methane. As demand for natural gas rises in the future, probably sharply, a greater demand will be put on our natural gas infrastructure. When this occurs, a closer look will be directed to options that were previously thought unviable. Another area that is currently being developed in anticipation of the future demand is GTL (gas-to-liquid) technology. There are many potentially rich gas fields that are not drilled because of the need to lay expensive steel pipes to transport the gas. If the field is very far away from the storage reservoir, the cost of the pipeline could discourage any speculators on the field. Transporting by ship, train, or truck is much less costly, but methane’s high volume as a gas prevents it from being transported in bulk. GTL is technology that allows the producer to convert the gas into a liquid fuel, allowing it to be transported much more compactly and hence more easily (Wilhelm et al., 2001). As mentioned before, liquid natural gas (LNG), is one way of accomplishing this.

However, the need to constantly keep LNG at a very low temperature is a drawback, sometimes a serious one. This leads to the other area of GTL, chemically reacting methane with other compounds, to produce a stable liquid methane-based fuel. This new liquid form is ready to be used for transportation, as well as to directly supply power to machinery, in the same manner gasoline is used. Producing GTL fuel is very costly at this time; however, because a methane-based liquid fuel has a large amount of positive characteristics, it is being heavily researched, and in the future, as costs go down, we should see more of these liquid hydrocarbon fuels.
1.2 Natural Gas

Natural gas is a combustible mixture of hydrocarbon gases. It is colorless, shapeless, and odorless in its pure form. As a safety measure, natural gas companies add an odorant, mercaptan, to the gas so that leaking gas can be detected. While natural gas is formed primarily of methane, it can also include ethane, propane, butane and pentane. The composition of natural gas can vary widely. Table 1.1 shows outlines the typical makeup of natural gas before it is refined. Natural gas is considered 'dry' when it is almost pure methane, having had most of the other commonly associated hydrocarbons removed. When other hydrocarbons are present, the natural gas is 'wet' (Thomas and Dawe, 2003).

The primary component of natural gas is methane (CH₄), the shortest and lightest hydrocarbon molecule. It may also contain heavier gaseous hydrocarbons such as ethane (C₂H₆), propane (C₃H₈) and butane (C₄H₁₀), as well as other sulphur containing gases, in varying amounts, see also natural gas condensate. Organosulfur compounds and Hydrogen sulfide (H₂S see acid gas) are common contaminants, which must be removed prior to most uses. Gas with a significant amount of sulfur impurities is termed "sour". Moreover, combustion of one cubic meter of commercial quality natural gas yields 38 MJ (10.6 kWh) (Yagi et al., 2005).

Methane is also an extremely efficient greenhouse gas which may contribute to enhanced global warming when free in the atmosphere, and such free methane, would then be considered a pollutant rather than a useful energy resource. However, methane in the atmosphere reacts with ozone, producing carbon dioxide and water, so that the greenhouse effect of released methane is relatively short-lived. As a pollutant, significant biological sources of methane are termites, cattle (ruminants) and cultivation (estimated emissions are 15, 75 and 100 million tons per year respectively) (Aguiar et al., 2005).

Natural gas is a fossil fuel like oil and coal, this means that it is, essentially, the remains of plants and animals and microorganisms that lived millions and millions of years ago. There are many different theories as to the origins of fossil fuels. The most widely accepted theory says that fossil fuels are formed when organic matter (such as the remains of a plant or animal) is compressed under the
earth, at very high pressure for a very long time. This is referred to as thermogenic methane (Lunsford, 2000). Similar to the formation of oil, thermogenic methane is formed from organic particles that are covered in mud and other sediment.

Table 1.1 The typical composition of natural gas before it is refined (Kvenvolden, 1995)

| Typical Composition of Natural Gas |
|----------------------------------|-----------------|
| Methane                          | CH₄             |
| Ethane                           | C₂H₆            |
| Propane                          | C₃H₈            |
| Butane                           | C₄H₁₀           |
| Carbon Dioxide                   | CO₂             |
| Oxygen                           | O₂              |
| Nitrogen                         | N₂              |
| Hydrogen Sulphide                | H₂S             |
| Rare Gases                       | A, He, Ne, Xe   |

This sediment and debris puts a great deal of pressure on the organic matter, which compresses it. This compression, combined with high temperatures found deep underneath the earth, break down the carbon bonds in the organic matter. As one gets deeper and deeper under the earth’s crust, the temperature gets higher and higher (Lunsford, 2000). At low temperatures (shallower deposits), more oil is produced relative to natural gas. At higher temperatures, however, more natural gas is created, as opposed to oil.

1.3 Natural Gas Conversion Technologies

Natural gas is found in considerable amounts in oil fields, often at remote locations, where the construction of pipelines to transport the gas is not economical. Under these circumstances, it is usually flared, vented, or pumped undergrounds
Thomas and Dawe, 2003). Therefore, finding an efficient process for utilizing such stranded gas receives considerable attention. In this direction, the conversion of methane, the main constituent of natural gas, into more valuable hydrocarbons is a topic of great interest. Up to now, indirect processes, involving partial oxidation and Fischer-Tropsch synthesis, are being used for this purpose. Recently many attempts have been made to develop a direct process for converting methane into higher hydrocarbons and the effective chemical activation of the methane molecule remains the most challenging step in such a process. In this research, an attempt is made to initiate a route for direct liquid hydrocarbons (C\textsubscript{5+}) production by catalytic reaction oxidation of methane with oxygen. Before that, various technology of methane conversion to higher hydrocarbon will be discussed further in this chapter to obtain a complete understanding about the processes involved.

The abundance of natural gas (the main constituent of which is methane), together with steadily depleting oil reserves, highlights methane conversion to higher hydrocarbons as an extremely attractive goal. Activation of methane is very challenging due to its refractory nature and has made this one of the most extensively investigated processes in catalysis. The processes of conversion of natural gas into liquid higher hydrocarbons products can be divided into two types: direct conversion and indirect conversion as shown in Figure 1.3. The primary step of the indirect route involves the production of syn-gas (a mixture of CO and H\textsubscript{2}) by steam reforming, partial oxidation, autothermal reforming; following this step the syn-gas is converted to hydrocarbons directly via Fischer–Tropsch catalysis or indirectly via other intermediates such as methanol.

The direct conversion processes utilize catalysts and specific synthesis routes to chemically transform the molecules of methane, the main component of natural gas, into more complex chained substances with heavier molecules. The desired products that can be obtained include the alcohols (mainly methanol), the olefins (ethylene and acetylene) and the aromatics (benzene, toluene and naphthalene). However, the high stability of the methane molecule creates a series of technical problems to make the chemical reactions involved viable. Thus, the research and development efforts of the direct conversion processes are focused on the
improvement of the catalysts in the elucidation of the mechanisms of reaction and the development of new equipment.

Taylor et al. (1988) explained that methane, oxygen, and hydrogen chloride (mixed CuCl, KCl, LaCl$_3$) are reacted over an oxyhydrochlorination catalysts. In the first stage produce methyl chloride and water. In second stage, the methyl chloride is converted to higher hydrocarbons, namely paraffins, olefins, aromatics and cycloparaffins, over zeolite, such ZSM-5, as shown by the chemical equation in (Equation 1.1 and Equation 1.2).

\[
\begin{align*}
\text{CuCl, KCl, LaCl}_3 \\
\text{CH}_4 + \text{O}_2 + \text{HCl} & \rightarrow \text{CH}_3\text{Cl} + \text{H}_2\text{O} \quad (1.1) \\
\text{CH}_3\text{Cl} & \rightarrow \text{Gasoline} + \text{HCl} \quad (1.2)
\end{align*}
\]

They reported that the conversion of methlychloride to gasoline range hydrocarbon (31-42 %) accurse under conditions similar to those for methanol to gasoline conversion. The oxyhydrochlorination catalysts was prepared in a non-aqueous solvent by successive impregnation of metal chloride salts onto a silica support. Final weight composition was as 41.7 % CuCl, 37.5% SiO$_2$, 11.5 % KCl and 9.4 % LaCl$_3$. the ZSM-% catalysts was obtained from Mobil Oil Cooperation in the ammonium form with silica to alumina ratio of 70:1 (Taylor et al.,1991). The ammonium form was converted to the hydrogen form by calcaning in air at 538 °C for 16 hrs.

Senkan (1987) has patent a process for oxidative pyrolysis of halogenated methanes in the gas phase and under non-flame conditions in the presence of oxygen which significantly reduces the formation of carbonaceous deposits, such as tars, solid carbon and soot, while maintaining high yields, in the order of 20 to 80 percent, of desired higher molecular weight hydrocarbon products. According to a preferred embodiment, the process of that invention may be a two step process wherein the first step involves the halogenation of methane using a halogen containing gas or oxyhalogenation using hydrogen halide in the presence of oxygen. Then in a second step, the halogenated methanes are oxidatively pyrolyzed under non-flame conditions.
in the presence of an oxygen containing gas. The process of that invention may also be a single step process wherein the methane halogenation and the oxidative pyrolysis of halogenated methanes are accomplished in a single vessel. According to that invention, oxygen converts to carbon monoxide hydrocarbon compounds which would otherwise result in the formation of carbonaceous deposits during conversion of halogenated methanes. Oxidative pyrolysis of the halogenated methanes yields higher molecular weight hydrocarbons such as acetylene and ethylene.

A process for oxidative pyrolysis of halogenated methanes in the presence of oxygen-containing gas under non-flame conditions is provided whereby the formation of solid carbonaceous materials is significantly reduced, while high yields of desired higher molecular weight hydrocarbons such as acetylene and ethylene are maintained. However, the oxyhydrochlorination process is not economical, because the chloride acid is very corrosive and the cost of special materials were replaced with carbon steel throughout (Cavani and Trifiro, 1997).

The indirect route is technically easier than that of the direct conversion processes. The technologies of the processes involved have been better studied and several pilot and commercial plants are already in operation (Wilhelm, 2001). The processes of indirect conversion are characterized by a preliminary stage of transformation of natural gas into synthesis gas - syngas - (a mixture of carbon monoxide - CO and hydrogen - H₂). Synthesis gas production requires either steam (steam reforming) or oxygen (partial oxidation) as a co-reactant. In either case, generation of these reactants is extremely energy and capital intensive and, as a result, the major cost of converting natural gas to liquid fuels lies in the initial synthesis gas production step. After being produced, the syngas is converted into liquid hydrocarbons through the Fischer-Tropsch Process (FT) (Gradassi and Green, 1995; and Vosloo, 2001).

On the other hand, hydrogen is perceived as an ideal energy carrier for a clean and sustainable energy future in the world, and fuel cells will play a significant role in this hydrogen based energy system as flexible, clean, and efficient energy devices suitable for use in a wide range of transportation and stationary/portable power generation applications. Among many potential sources for hydrogen
Figure 1.3  Methane to liquid hydrocarbons conversion routes
generation, natural gas, which is clean hydrocarbon fuel, abundant, and well-distributed, is considered to be one of the ideal fuels for hydrogen source for fuel-cell stationary applications. Many companies are developing natural-gas fuel-cell systems for residential/stationary applications and commercial/industrial markets. Reforming natural gas is a well-established technology in the petrochemical and fertilizer industries for the production of hydrogen for use in the manufacture of ammonia, methanol, and other chemical products (Lee et al., 2005) This technology has been reviewed in detail and includes three basic processes: steam reforming (SR), partial oxidation reforming (POR), and auto thermal reforming (ATR). In recent years, the catalytic ATR process has received much research and development attention as a viable process for hydrogen generation for fuel-cell systems because it offers advantages of simpler design (smaller and lighter unit), lower operating temperature (easier start-up and a wider choice of materials), and flexible load following characteristic as compared to the SR process. It also has higher energy efficiency than the POR process (Lee et al., 2005).

The methane-steam reforming reactions are strongly endothermic and the thermodynamic equilibrium is favored by high temperature. The conventional steam reformers are mainly fixed bed catalytic reactors. The catalyst is normally loaded into a number of tubes placed in a furnace, which operates at high temperature varying from 850 to 1100 K. The reactors suffer from uniform distribution of heat fluxes and profound effect of high temperature on the tubes and catalyst life. Moreover, the diffusion limitations are severe with very low effectiveness factor in the order of $(10^{-2}–10^{-3})$ (Abashar, 2004). In addition, the reactions produce significant quantities of carbon dioxide (important greenhouse gas), which is harmful to the environment.

In recent years various experimental and theoretical attempts have been made to improve different aspects of processing methane to produce hydrogen. Considerable attention has been paid to the fluidized bed membrane reactors (FBMRs) as multi-functional reactors (Abashar, 2004). Their main advantages are: shift of the thermodynamic equilibrium, enhancement of methane conversion, simultaneous reaction and separation of hydrogen, elimination of diffusion limitations, good heat transfer capability and a more compact design (Laosiripojana
and Assabumrungrat, 2005). Also, the carbon dioxide reforming of methane, the so-called dry reforming of methane (CO₂ reforming) has gained increasing importance. The process of great significance for environmental protection, it enables the transformation of CO₂ into synthesis gas (syngas). Recently, several studies have shown that the performance of the fixed bed catalytic reactors has improved significantly by introduction of the dual-functionality via structured pattern (either mixed or layered configuration) of the catalyst bed. The purpose of these patterns is to couple the reactions in different ways to achieve certain degree of integration of heat, further shift of thermodynamic equilibrium and simultaneous production of more than one product (Abashar, 2004).

The following sub-chapters will deal with the ‘‘GTL’’- technology as well as the oxidative coupling of methane (OCM), where zeolites and related MgO based material respectively have been demonstrated to be superior catalysts.

1.3.1 Gas to Liquids (GTL) Technology

GTL technology is based on the conversion of natural gas to liquid fuels in three stages: synthesis gas generation, production of heavy-chain hydrocarbons by Fischer-Tropsch synthesis and heavy fraction hydrocracking for production of useful compounds such as naphtha, diesel and lubricants (Figure 1.4) (Aguiar et al., 2005; and Yagi et al., 2005). Although the three stages of the GTL process by indirect means have been individually well studied and are available for commercialisation, an optimal combination that permits the reductions of costs of the commercial production plants still does not exist. Additionally, the synthesis gas generation stage corresponds to the greatest costs in investments and operation, being responsible for around 50–75% of the capital costs (Vosloo, 2001). Therefore, many large companies are seeking to optimize the synthesis gas generation stage, in order to make the GTL technology commercially viable (Wittcoff et al., 2004).
On the other hand, fuels production directly from syngas (in former times obtained from coal) has been reported by Fischer and Tropsch in 1923 for the first time (Wilhelm et al., 2001), using an alkali-promoted iron catalyst. Fuels manufactured via the Fischer–Tropsch route reveal an excellent quality since they consist mainly of linear paraffins and olefins and do not contain sulfur and aromatics. A Co-containing catalyst is applied for the production of heavy paraffins via the Fischer–Tropsch route starting with natural gas, a technology developed by Shell and named the “Shell Middle Distillate Synthesis (SMDS)” route (Lunsford, 2000). In addition, diesel fuel (or gasoline) is produced by hydrocracking of the more or less sulfur and nitrogen-free wax obtained through the SMDS process using noble metal containing zeolites. The more restricted fuel specifications currently introduced in order to reduce the environmental impact of hazardous emissions represent a driving force with respect to an increased use of fuels prepared via the Fischer–Tropsch route as a blending component of the gasoline and diesel pools in the future (Aguiar et al., 2005). Figure 1.5 is a block flow diagram of the GTL process.
Besides the SMDS technology, an alternative has been presented by SASOL/Chevron termed as the “Slurry-Phase-Distillate” process, again based on the Fischer–Tropsch route producing wax (using a Co-containing catalyst) followed by a hydrocracking step in order to get diesel or gasoline (Espinoza et al., 1999). The methanol to gasoline (MTG) plant in New Zealand has been combined with a methane steam reforming unit for production of synthesis gas and a methanol plant to produce gasoline from natural gas. The process economics can be improved considerably by a clever combination and close integration of the different steps. Finally, ExxonMobil has introduced the so-called “Advanced Gas Conversion for the 21st Century” (AGC-21) technology, again based on the Fischer–Tropsch route (Ashley et al., 2003; and Wittecoff, et al., 2004).

In any manner, the reduction of costs of any stage is still the principal objective of all companies developing GTL. The use of catalytic membranes and compact reformers represents considerable advances in the area. Another possibility is in the elimination of the isomerization unit, which would occur if the Fischer–Tropsch catalysts were able to generate isomerized products. The addition of
Bronsted acid sites to the traditional cobalt catalysts appears to be an interesting research option that is still under-explored. This catalyst was tested and refined to improve performance; thus creating an ultra-stable catalyst with high activity and selectivity. Using an integrated simulation model for reforming and F-T synthesis, designers developed detailed mass balance flowsheets, engineering line diagrams, utility line diagrams, plant layouts, process and mechanical specifications of all equipment and instrumentation and comprehensive schedules of all bulk materials.

1.3.2 Oxidative Coupling of Methane

Conversion of methane into liquid products is traditionally achieved via steam reforming to produce CO and H₂, followed by transformation of these diatomic molecules into oxygenates and higher hydrocarbons. Because the energy input required for steam reformation is exorbitant, alternative routes to methane conversion have been pursued. One approach which leads to direct formation of C₂ products is oxidative coupling of methane (OCM).

This oxidative coupling of methane (OCM) is a promising route for the conversion of natural gas to ethylene that can be used for the production of petrochemicals or fuel. The reaction takes place in the presence of catalysts at temperatures from 650 to 850°C (Zaman, 1997). In the oxidative coupling reaction, CH₄ and O₂ react over a catalyst at elevated temperatures to form C₂H₆ as a primary product and C₂H₄ as a secondary product. The reaction network is interesting from a fundamental perspective because it is an example of a heterogeneous–homogeneous system.

Oxides of alkali, alkaline earth and rare earth metals, singly or in combination, catalyze the reaction to the desired path. Maitra (1993) analyzed the performance of the different types of OCM catalysts and concluded that only the basic oxides constitute good catalysts. According to this mechanism, the methane activation proceeds via hydrogen abstraction on a basic O²⁻ site producing CH⁻₃ which, in a secondary reaction with oxygen, produces CH₃⁻, simultaneously
converting $O_2$ to $O^-_2$. Methyl radicals that are formed at the surface of the catalyst enter the gas phase where they couple to form ethane. Over basic oxides catalysts, it is indeed observed that secondary reactions of ethane are responsible for ethylene formation (Martin and Mirodatos, 1995).

In addition to coupling, the gas phase radicals may enter into chain reactions that result in the formation of CO and subsequently CO$_2$. Isotopic labeling experiments have demonstrated that at small conversion levels, most of the CO$_2$ is derived from CH$_4$, but at commercially significant conversion levels, C$_2$H$_4$ would be the dominant source of CO$_2$ (Martin and Mirodatos, 1995). Additional experiments have shown that this occurs mainly via a heterogeneous reaction. One of the challenges in catalyst development is to modify a material so that the secondary reaction of C$_2$H$_4$ will be inhibited while the activation of CH$_4$ will still occur. There is no inherent reason that these two reactions should take place on the same types of sites. A complex model of the OCM reaction over a lanthanum basic oxides catalyst is summarized in Figure 1.6 (Mleczko et al., 1995).

Figure 1.6 Reaction scheme of the OCM over the basic oxides catalyst (Mleczko et al., 1995)

The scheme includes the nine heterogeneously catalyzed and one homogeneous non-catalytic (reaction 8) reactions:
(1) total oxidation of methane to carbon dioxide,
(2) oxidative coupling of methane to ethane,
(3) partial oxidation of methane to carbon monoxide,
(4) oxidation of carbon monoxide to carbon dioxide,
(5) oxidative dehydrogenation of ethane to ethylene,
(6) oxidation of ethylene to carbon monoxide,
(7) steam reforming of ethylene,
(8) thermal dehydrogenation of ethane to ethylene,
(9/10) conversion of CO to CO₂ and vice versa

1.3.3 Hydrogen from Methane Conversion Reaction

Hydrogen is used as both a chemical feed and a fuel, and is generally produced by steam reforming of hydrocarbons, especially natural gas, from water gas shift reactions, from catalytic reforming of petroleum stocks and by electrolysis. It has been reported that hydrogen can be formed by the decomposition of methane over iron catalysts. This process results in the formation of coke on the catalyst, which ultimately destroys the activity of the catalyst. It may be assumed that decomposition of methane produces hydrogen and carbon black by the following single reaction (Cho et al., 2004):

$$\text{CH}_4 + 75.3 \text{ (kJ/mol)} \rightarrow \text{C} + 2\text{H}_2 \quad (1.3)$$

According also to Cho et al. (2004), the total enthalpy of methane decomposition at 1873 °C is 182.7 kJ/mol, and the energy related to carbon mass varies approximately between 4 and 7 kW h per kg of carbon produced or 1 and 1.9 kW h per normal cubic meter of hydrogen produced.

In the case of OCM and oxidative dehydrogenation (ODH) it is very likely that a serious problem will be faced when trying to extract the intrinsic kinetic constants of elementary heterogeneous interactions from experimental data. The rates
of reactant conversion and product formation are a complex combination of terms attributed to numerous elementary reactions localized both on the catalyst surface and in the gas phase. However, such a conversion is highly endothermic; under the high temperature reaction conditions required therefore, control of the reaction to prevent the formation of unwanted by-products is difficult.

As Sinev et al. (2003) demonstrated earlier, free-radical gas-phase processes play a very important role in product formation during light alkane oxidation. The development of chain process in the gas phase leads to the formation of various radical and molecular species further transformations of which can produce hydrogen. First of all, alkyl radicals $C_nH_{2n+1}$ formed as primary radical species during alkane activation in heterogeneous or homogeneous steps can undergo consecutive scission evolving H-atom which then reacts with any H-containing molecules RH (first of all, with initial alkane) with $H_2$ molecule formation:

$$[O]_S + C_nH_{2n+2} \rightarrow [OH]_S + C_nH_{2n+1} \quad (1.4)$$

$$X + C_nH_{2n+2} \rightarrow XH + C_nH_{2n+1} \quad (1.5)$$

$$C_nH_{2n+1} \rightarrow H + C_nH_{2n} \quad (1.6)$$

$$RH + H \rightarrow R + H_2 \quad (1.7)$$

where $[O]_S$ is the active surface site; $X$ is any gas particle which has an affinity to hydrogen atom (e.g. $O_2$, $OH$, $HO_2$, $H$, alkyl, alkoxy, alkylperoxy species, etc.).

As can be seen, the sequence of steps (1.4), (1.6) and (1.7) leading to the formation of at least one olefin and one $H_2$ molecules and to the development of homogeneous chain process starts from the oxidative abstraction of H-atom from alkane molecule by a surface active site. If a chain initiation takes place in the gas phase, the first step (3) (in this case $X = O_2$) is also an oxidative H-atom abstraction. The same can be said about alkane molecule reaction (1.5) with any oxidative particles present in the gas phase during a developed chain reaction. In other words, this sequence of steps can be considered as an oxidative process leading to molecular hydrogen forming in parallel with olefin. In the work dedicated to the OCM process, Sinev (2003) explained the formation of high concentrations of molecular hydrogen...
during methane oxidation at moderate temperatures (below 650 °C) by the formation and rapid decomposition of formaldehyde.

The overall reaction of oxidative coupling is:

\[ 4\text{CH}_4 + \text{O}_2 \rightarrow 2\text{C}_2\text{H}_6 + 2\text{H}_2\text{O} \]  
(1.8)

followed by dehydrogenation of ethane to ethylene:

\[ \text{C}_2\text{H}_6 \rightarrow \text{C}_2\text{H}_4 + \text{H}_2 \]  
(1.9)

However the detailed reaction mechanism is very complex. The many possible side reactions produce other oxidation products such as CO and CO\(_2\). Although hydrogen is also a product of the OCM reaction, it is normally converted back to other products via complex reaction mechanism.

In the conditions of optimal production of olefins during oxidation of light alkanes over typical OCM catalysts molecular hydrogen forms as one of the major products. Variations of kinetic features depending on the initial alkane, catalyst and reaction conditions are indicative for the existence of multiple pathways of hydrogen formation. If almost total conversion of oxygen takes place in the front part of the reactor, non-oxidative dehydrogenation (NODH) process can proceed in the remaining part of catalyst bed. Over some catalysts hydrogen formation can also accompany the intense coking. In addition to non-oxidative routes, some oxidative processes, including those proceeding in the gas phase, can lead to the production of hydrogen which in this case is accompanied by both additional olefin formation and total oxidation. However, reactions followed by the hydrogen oxidation by oxygen and hydrogenation with primarily formed olefins decreased the yield of hydrogen in the OCM final reaction products. Further elucidation of the reaction pathways can help to improve the target olefin production in the OCM reaction.

On the other hand, oxidative dehydrogenation (ODH) of light alkanes attracts a considerable attention as a potentially efficient way to produce olefins from relatively cheap and abundant feedstocks. The main usually discussed advantage of
ODH over NODH of the same alkanes is the absence of thermodynamic limitations for per-pass olefin production since in the case of NODH an upper limit of yield determined by equilibrium cannot be exceeded. The thermodynamics of CH₄ conversion is shown in Figure 1.7. Coke formation by reaction (1) in Figure 1.7 is most favorable, it can become one of the steps whereby supported noble metal catalysts can be inactivated.

![Thermodynamics of some methane conversion reactions which produce hydrogen](Gesser and Hunter, 1998)

In principle, the removal of hydrogen from the reaction system by any means helps to eliminate the thermodynamic limitations for olefin formation. For instance, selective in situ burning of hydrogen formed over NODH catalyst enables to increase olefin yields. However, catalytic ODH is considered as the most promising way to avoid thermodynamic limitations and necessity of external heating during the
production of olefins from light alkanes. Indeed, if oxidant (e.g. molecular oxygen) is added to the feed gas the process becomes thermodynamically favorable at any level of alkane conversion and olefin yield. The only condition which has to be provided is water formation instead of H₂.

In real practice, however, neither water, nor hydrogen are usually measured experimentally when the reaction mixture is analyzed by on-line gas chromatography (GC). An accurate analysis of water requires additional complications of sampling system. As to the GC analysis of molecular hydrogen, some problems are discussed below. As a result, the analysis of experimental sections of publications dealing with ODH of light alkanes shows that in most cases in these studies only carbon balance is a subject of concern and the fate of hydrogen abstracted from alkane molecule cannot be traced because neither H₂, nor water are analyzed. On the other hand, it is well known that substantial amount of hydrogen are formed during the oxidative coupling of methane (OCM) which is relative to ODH process (both reactions require elevated temperatures; they both proceed via the abstraction of H-atom from C–H bond; OCM catalysts are very efficient in ODH). The detailed studies of hydrogen formation during oxidation of C₁–C₄ alkanes over a series of typical ODH catalysts undertaken in some OCM works indicates that the reaction pathways are much more complicated than it has been believed previously. However, the analysis of product yields shows that even if NODH is the only process leading to the formation of olefin, hydrogen production exceeds by far the value corresponding to the formation of olefin and its possible sequential overoxidation. This indicates that certain pathways of hydrogen formation become more important at increasing length of carbon chain in hydrocarbon molecules. The trends described above are suggestive for an existence of multiple pathways for hydrogen formation in the conditions of alkane oxidation in OCM reactions. These pathways should follow different kinetic regularities when reaction parameters, such as temperature, residence times and reactant concentrations, are varied.

Moreover, since the highest concentrations of hydrogen in the reaction mixture are observed in the conditions close to optimal olefin formation, the elucidation of the process pathways is worth for further optimization of target product yield. In fact, one possibility is that a substantial fraction of olefin forms
simultaneously with H₂ via NODH over reduced catalyst at the expense of heat produced in total oxidation reaction (in which the most part of oxygen is consumed). If so, there is no practical reason to run the reaction in the oxidative mode and a more economical way to supply heat for NODH should be found. On the other hand, if hydrogen formation is a result of some by-processes, special efforts should be mounted to suppress them. In the latter case, monitoring of H₂ concentration in the reaction mixture is a good way to control the efficiency of these efforts.

Under the usual reaction conditions for the OCM, H₂ is a major reaction product although early studies failed to observe or seemed to have overlooked this due to analytical difficulties, as mentioned in above. Therefore, not many studies seem to have reported the production of H₂ among the numerous studies on the OCM (Choudhary et al., 1997 and Lacombe et al., 1994). H₂ can be formed via a number of pathways, such as steam reforming reactions, the water-gas shift reaction, homogeneous gas-phase methane oxidation, and decomposition of ethyl radicals (Heracleous and Lemonidou, 2004). From a detailed study on the OCM over MgO, Hargreaves et al. (2002) have reported that the water-gas shift reaction is an important H₂ source and that partial oxidation of hydrocarbons becomes more significant at high flow rates and low O₂ conversions; also involved is thermal cracking of ethane to ethene. Hutchings et al. (2002) have proposed from a study on the OCM over MgO, La₂O₃ and Sm₂O₃ that gas-phase radical oxidation which is linked directly to the formation of carbon oxides is important but dehydrogenation of ethane is discounted as a major route due to the thermodynamic limitation. Possible reactions producing H₂ in the OCM process are listed as follows (Hong and Yoon, 2001):

Steam reforming of hydrocarbons:

\[
\begin{align*}
\text{CH}_4 + \text{H}_2\text{O} &= \text{CO} + 3\text{H}_2; \ H_2: \text{CO} = 3 \\
\text{C}_2\text{H}_6 + 2\text{H}_2\text{O} &= 2\text{CO} + 5\text{H}_2; \ H_2: \text{CO} = 2:5 \\
\text{C}_2\text{H}_4 + 2\text{H}_2\text{O} &= 2\text{CO} + 4\text{H}_2; \ H_2: \text{CO} = 2
\end{align*}
\]

Partial oxidation of hydrocarbons:
\[ \text{CH}_4 + \frac{1}{2}\text{O}_2 = \text{CO} + 2\text{H}_2; \enspace \text{H}_2: \text{CO} = 2 \quad (1.13) \]
\[ \text{C}_2\text{H}_6 + \text{O}_2 = 2\text{CO} + 3\text{H}_2; \enspace \text{H}_2: \text{CO} = 1:5 \quad (1.14) \]
\[ \text{C}_2\text{H}_4 + \text{O}_2 = 2\text{CO} + 2\text{H}_2; \enspace \text{H}_2: \text{CO} = 1 \quad (1.15) \]

CO\text{2 reforming of hydrocarbons:}

\[ \text{CH}_4 + \text{CO}_2 = 2\text{CO} + 2\text{H}_2; \enspace \text{H}_2: \text{CO} = 1 \quad (1.16) \]
\[ \text{C}_2\text{H}_6 + 2\text{CO}_2 = 4\text{CO} + 3\text{H}_2; \enspace \text{H}_2: \text{CO} = 0:75 \quad (1.17) \]
\[ \text{C}_2\text{H}_4 + 2\text{CO}_2 = 4\text{CO} + 2\text{H}_2; \enspace \text{H}_2: \text{CO} = 0:5 \quad (1.18) \]

Water-gas shift reaction:

\[ \text{CO} + \text{H}_2\text{O} = \text{CO}_2 + \text{H}_2 \quad (1.19) \]

In summary, it is proposed that the major pathways for the production of H\text{2} over the OCM catalysts are the dehydrogenation of ethane, steam reforming and partial oxidation of ethane and ethene which accompany simultaneous production of CO.

### 1.4 Heterogeneous Catalysis and Catalyst

A catalyst is a substance which controls the rate of reaction without itself undergoing a permanent chemical change and the process is called catalysis. The modern concept of catalysis was defined by Berzelius as follows: “Catalysis is a process whereby a reaction occurs faster than the uncatalyzed reaction, the reaction being accelerated by the presence of a catalyst” (Krische, 2005; Somorjai and McCrea, 2000; Haller, 2003; and Ponec, 1998).

There are two types catalyst, which are positive catalyst and negative catalyst or inhibitor. A positive catalyst increases the rate of reaction by lowering the energy of activation. Thus, in the presence of a positive catalyst, the greater fraction of the total molecule will posses lower energy of activation and collided successfully in a
short period of time, there by increasing the rate of reaction. A positive catalyst functions by providing an alternate path to the reaction or by the formation of a transition (intermediate) compound having low energy of activation as shown in Figure 1.8. The activation energy of this path is lower. As a result the rate of reaction is increased. A negative catalyst retards the rate of reaction. A negative catalyst does not lower the energy of activation; rather it is combined with reactant molecule thus decreasing the number of colliding reactant molecules. This decreases the effective collisions, hence the rate of reaction (Fogler, 1999).

Catalysis can be classified as homogeneous catalysis, in which only one phase is involved, and heterogeneous catalysis, in which the reaction occurs at or near an interface between phases (Bond, 2000; and Chen et al., 2005a). The choice for a certain catalyst for a catalytic conversion is not only determined by the reaction itself but also by the industrial process (Taguchi and Schuth, 2005). For example, heterogeneous catalysts are used for the production of bulk chemicals because the solid catalyst materials are unmixable with products. This facilitates the separation of products and catalyst material, especially if gaseous products are involved. Consequently, the reaction can be performed under continuous flow conditions which permits the scaling up of production processes to achieve high rates. This advantage of heterogeneous catalysis is of exceptional importance because it allows the production of gasoline, fuel oil and other bulk chemicals on a large scale which is essential to provide sufficient bulk chemicals to satisfy the vast demands of the world market (Holzwarth et al., 2001; Blaser, 2000; and Kerby et al., 2005). Because most of the work presented in this thesis focuses on zeolite material and MgO based OCM catalyst, a brief description of these catalysts is presented in the next sections.
1.4.1 Zeolite

1.4.1.1 History and Zeolite Development

The word “Zeolite” was first used by a Swedish mineralogist Axel Cronstedt. In 1756, he discovered the very first zeolite mineral “stilbite”. This mineral visibly lost water when heated. Accordingly, he named this class of mineral “zeolite” from the classical Greek words “zeo”, meaning to boil, and “lithos”, meaning stone. Since then, about 40 different kinds of natural zeolites have been identified (Erdem et al., 2004). They vary in crystal structure and chemical composition, and some physical properties as well. Today, most natural zeolites have been successfully synthesized in laboratories or in commercial plants. Besides natural zeolites, man-made or synthetic zeolites have also added many new members to the zeolite family. Scientists have synthesized many zeolites that do not exist naturally or at least have not been discovered on the earth (Casci, 2005).
Zeolite is defined by Smith (1963) as “an aluminosilicate with a framework structure enclosing cavities occupied by large ions and water molecules, both of which have considerable freedom of movement, permitting ion-exchange and reversible dehydration” (Murakami et al., 1986). Other definitions can also be found. Jacobs (1977) gave the following definition: “Zeolites as synthesized or formed in nature are crystalline, hydrated alumino-silicates of group I and II elements. Structurally, they comprise a framework based on an infinitely extending three-dimensional network of SiO₄ and AlO₄ tetrahedra linked together through common oxygen atoms” (Jeanette, 1980). Szostak (1989) stated that “structurally, zeolite is a crystalline aluminosilicate with a framework based on an extensive threedimensional network of oxygen ions” (Ribeiro et al., 1995). Recently, Corma (2003) defined zeolite as “crystalline silicalites and aluminosilicates linked through oxygen atoms, producing a three-dimensional network containing channels and cavities of molecular dimensions.” Although the four definitions are stated differently, the main characteristics of a zeolite are either clearly expressed or implied as a crystalline material of aluminosilicate featured by a three-dimensional microporous framework structure built of the primary SiO₄ and AlO₄ tetrahedra, and ion-exchange capability.

Nowadays, zeolites are available on a large scale and in a variety of applications. The major use of zeolites is as ion exchangers in laundry detergents where they remove calcium and magnesium from water by exchanging it for sodium present in the zeolite. Furthermore, zeolites are applied as adsorbents in the purification of gas streams to remove water and volatile organic species, and in the separation of different isomers and gas-mixtures. Moreover they are applied in the clean up of radioactive wastes. However, in this thesis the focus will entirely be on the application of zeolites as catalysts for the conversion of hydrocarbons. Catalysis by zeolites with focus on hydrocarbon conversion and formation covers, nowadays, a broad range of processes related to the upgrading of crude oil and natural gas. This includes, among others, fluid catalytic cracking (FCC), hydrocracking, dewaxing, aliphate alkylation, isomerisation, oligomerisation, transformation of aromatics, transalkylation, hydrodecyclisation as well as the conversion of methanol to hydrocarbons (Stocker, 2005). All these conversions are catalyzed by zeolites or related microporous materials, based both on the acid properties and shape-selective behavior of this type of materials.
The ordered, crystalline structures imply that the micropores in zeolites have very well-defined dimensions and connectivities. In addition, the framework composition can be tuned to enhance chemical selectivity. These features combine to ensure that zeolites form a very important category of cheap, highly reproducible size and shape selective molecular sieves and adsorbents which find widespread use in industry (Weitkamp, 2000).

Moreover, as extensively used porous materials, zeolites show marked advantages over other solid materials (Stocke... and Corma, 2003):

- Well defined structure which could be clearly related to the activity and selectivity;
- Well defined inner pores in which active species can be hosted;
- Adjustable framework composition and cations associated with different stability; hydrophilicity/hydrophobicity and acid-based properties
- A large amount of structures that can be chosen as shape-selective catalysts for different reactions.

1.4.1.2 Structure of Zeolites

The elementary building units of zeolites are SiO$_4$ and AlO$_4$ tetrahedra. Adjacent tetrahedra is linked at their corners via a common oxygen atom, and this results in an inorganic macromolecule with a structurally distinct three-dimensional framework. It is evident from this building principle that the net formulae of the tetrahedra are SiO$_2$ and AlO$_2^-$, i.e. one negative charge resides at each tetrahedron in the framework which has aluminum in its center (Ali et al., 2003). The framework of a zeolite contains channels, channel intersections and/or cages with dimensions from ca. 0.2 to 1 nm. So, aluminosilicates have negatively charged oxide frameworks (one charge per framework Al$^{3+}$) which require charge-balancing by cations. Typical cations include the alkaline (Li$^+$, Na$^+$, K$^+$) and the alkaline earth (Mg$^{2+}$, Ca$^{2+}$, Ba$^{2+}$) ions, quaternary ammonium ions, protons (in the acid form of zeolites), and the rare...
earth and noble metal ions. The cations are quite mobile and may be exchanged by other cations, which determine the ion-exchange properties of the zeolites (Nowinska et al., 2003).

Zeolites are crystalline networks of alumino-silicate, where the structural formula of zeolites is best expressed for the crystallographic unit cell as (Hashimoto, 2003):

$$M_{x/n}[(\text{AlO}_2^-)_x(\text{SiO}_2)_y].w\text{H}_2\text{O} \quad (1.20)$$

Where M is the cation of valence n, the portion with [ ] represents the framework composition. The sum (x + y) is the total number of tetrahedral in the unit cell. The ratio x/y must be smaller than or equal to 1, since AlO$_2^-$ tetrahedral can only join to SiO$_2$ tetrahedra according to the Lowenstein rule. w is the number of water molecules per unit cell. The water in many zeolites can be reversibly removed by calcinations, leaving an open host structure.

Structurally, zeolites are built of primary and secondary building units. The primary unit is simply the SiO$_4$ or AlO$_4$ tetrahedron. Si or Al atom sits at the center of the tetrahedron with 4 oxygen atoms co-valently bonded to the centered Si or Al atom (so-called T-atom). From this primary unit, a number of secondary building units can be built by a linkage through the oxygen atom covalent bonding, which is called an oxygen bridge (Weitkamp, 2000). The secondary building units are featured by simple geometric shapes such as those shown in Figure 1.9. A zeolite structure is finally constructed from the secondary units. A pore channel system is formed during the systematic packing of the secondary units (Ribeiro et al., 1995). A schematic representation of the structuring process of a zeolite is shown in Figure 1.9.

Furthermore, zeolites were traditionally used as highly selective adsorbents, ion exchangers and catalysts with high activity and selectivity in a wide range of reactions. The unique properties of zeolites arise from their uniformity in pore size and the chemical composition. The pore size of zeolites was determined by the number of T atoms in the ring openings, where T is Si$^{4+}$ or Al$^{3+}$. Zeolites with pores comprising of 8, 10, and 12 T atoms have historically been classified as small (8-member ring), medium (10-member ring), and large-pore zeolites (12-member ring).
respectively (Weitkamp, 2000). These pores may extend in one-dimensional tunnels, two-dimensional intersecting cages and, finally, three-dimensional connected channel system of nanometer scale networks. This microporous pore system renders zeolites high surface area and allows zeolites to recognize, discriminate, and organize molecules with precisions that can be less than 1 Å (Roldan et al., 2005). The molecular shape selectivity of zeolites results from the interaction of adsorbed molecules with zeolite channels or cages of atomic size. In addition, the characteristics of some typical zeolites are listed in Table 1.2.

**Figure 1.9** Schematic representation of building zeolites (Rabo, 1976)
Table 1.2: Characteristics of some typical zeolite porous material (Weitkamp, 1998)

<table>
<thead>
<tr>
<th>Zeolite</th>
<th>Number of rings</th>
<th>Pore size (Å)</th>
<th>Pore/Channel Structure</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>8-membered oxygen ring</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Erionite</td>
<td>8</td>
<td>3.6 x 5.1</td>
<td>Intersecting</td>
</tr>
<tr>
<td><strong>10-membered oxygen ring</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>ZSM-5</td>
<td>10</td>
<td>5.1 x 5.5</td>
<td>Intersecting</td>
</tr>
<tr>
<td></td>
<td></td>
<td>5.3 x 5.6</td>
<td></td>
</tr>
<tr>
<td>ZSM-11</td>
<td>10</td>
<td>5.3 x 5.4</td>
<td>Intersecting</td>
</tr>
<tr>
<td><strong>Dual pore system</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ferrierite</td>
<td>10,8</td>
<td>4.2 x 5.4</td>
<td>One dimensional</td>
</tr>
<tr>
<td></td>
<td></td>
<td>3.5 x 4.8</td>
<td>10:8 intersecting</td>
</tr>
<tr>
<td>Mordenite</td>
<td>12</td>
<td>6.5 x 7.0</td>
<td>One dimensional</td>
</tr>
<tr>
<td></td>
<td>8</td>
<td>2.6 x 5.7</td>
<td>12:8 intersecting</td>
</tr>
<tr>
<td><strong>12-membered oxygen ring</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>ZSM-12</td>
<td>12</td>
<td>5.5 x 5.9</td>
<td>One dimensional</td>
</tr>
<tr>
<td>Faujasite</td>
<td>12</td>
<td>7.4</td>
<td>Intersecting</td>
</tr>
<tr>
<td></td>
<td></td>
<td>7.4 x 6.5</td>
<td>12:12 intersecting</td>
</tr>
<tr>
<td><strong>Mesoporous system</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>VPI-5</td>
<td>18</td>
<td>12.1</td>
<td>One dimensional</td>
</tr>
<tr>
<td>MCM41-S</td>
<td>-</td>
<td>16-100</td>
<td>One dimensional</td>
</tr>
</tbody>
</table>

1.4.1.3 Mechanisms of the Shape Selectivity

In particular, zeolites usually show specific selectivity in some reactions due to their microporous properties. Because the pores of the zeolites are similar to many organic molecules of practical interest, it became possible to design novel catalysts which control the progress of the reactants and products through them via selecting the molecules by their size and shape, so called shape selective catalysts (Ramaswamy, 2003). It is generally believed that the majority of the active sites is located in the pores of zeolite (Corma, 2003).
Typically, five fundamental steps are involved in an overall reaction using zeolite as a catalyst: (i) diffusion of molecules from gas phase into the pores of the zeolites; (ii) adsorption of molecules on active sites; (iii) conversion of reactants molecules into product molecules; (iv) desorption of product molecules from active sites and eventually; (v) diffusion of product molecules into gas phase from the pores of the zeolite. The shape selectivity of the zeolite for a specific reaction may be possibly involved in step (i), (iii) or / and (v) (Krishna and Baur, 2003).

Based on different controlling steps, the shape selectivity of zeolites usually observed can be classified into three different types, including reactant shape selectivity, product shape selectivity and transition state selectivity, which are described in Figure 1.10.

![Diagram of shape selectivity](image)

**Figure 1.10** Schematic diagram of shape selectivity of zeolite (Krishna and Baur, 2003).

Reactant shape selectivity can be observed in the case of different participating reactant molecules with smaller and bulkier diameters compared to the pore entrance of zeolite. Reactants with smaller kinetic diameters can penetrate into
the interior pores of zeolite and access the active sites located in the pores of the
zeolite. Reactants with larger diameter, however, cannot diffuse into the pores of
zeolite and the reaction with bulky reactant molecules involved can be encumbered.

Product shape selectivity occurs when some of the reaction products cannot
escape from the zeolite due to their size or shape. Then these molecules can undergo
a secondary reaction to form molecules that are able to leave the catalyst. Transition
state selectivity is observed when both the reactant and product molecules fit well
within the pores of the zeolite, while the reaction intermediates are larger than them
and are spatially constrained either by their size or by orientation.

1.4.1.4 ZSM-5 Zeolite Catalyst

The type of zeolite catalyst used in this project is called Mobil Synthetic
Zeolite-5 (ZSM-5), which was developed by Argauer and Landolt in 1972 (Gayubo
et al., 2003). Since its inception, ZSM-5 has been widely used for hydrocarbon inter
conversion in the petroleum industry. ZSM-5 zeolites in protonic type (H-ZSM-5)
have been extensively used in acid catalyzed reactions. H-ZSM-5 zeolites can be
synthesized with a broad range of Si-Al ratio from 6 to infinity. In principle, the acid
strength and acid types are the key properties of zeolites, which play a crucible role
in the activity and selectivity of the zeolites. The range of zeolite-catalyzed reactions
can be extended by the incorporation of metal atoms both inside and outside the
zeolite framework (Goursot, et al. 2003).

The topology of the zeolite framework is given by a unique three-letter code,
which is not related to the composition of the material. Generally, based on the pore
openings, zeolites are referred to as small (8-member ring), medium (10-member
ring) and large (12- member ring) pore zeolites. Thus, ZSM-5 is a medium pore
zeolite materials with Mobil Five (MFI) topology (Rabo, 1976). The MFI structure is
built up by 5-1 secondary building units ( SBU; the smallest number of TO₄ units,
where T is Si or Al, from which zeolite topology is built) which are linked together
to form a chain (Figure 1.11) and the interconnection of these chains leads to the
formation of the channel system in the structure (Klinowski and Barrie, 1988). The MFI structure has a three-dimensional pore system consisting of sinusoidal 10-ring channels (5.1 x 5.5 Å) and intersecting straight 10-ring channels (5.3 x 5.6 Å) and these two different channels are perpendicular to each other and generate intersections with diameters of 8.9 Å (Hashimoto, 2003).

For the Methanol to Gasoline (MTG) process, it is the pores created by these 10-oxygen rings, along with the zig-zag pores intersecting them that are essential to the formation of products that are desirable components of gasoline (Grobet, 1988). An 8-oxygen ring zeolite will not produce molecules with 6 or more carbons as molecules of this size will not fit into the small pores of these zeolites. The large pores of a 12-oxygen ring zeolite produce large amounts of C-11 and C-12 compounds, which are undesirable products for gasoline range hydrocarbons (Rabo, 1976).

On the other hand, most of ZSM-5 catalysts are used in oil refining and gas-conversion processes, such as the conversion and upgrading of the various fractions into transportation fuels, methanol-to-gasoline, conversion of syngas, light paraffins and olefins into gasoline and gasoil (Kerby et al., 2005). A huge interest in ZSM-5 is due to its unique properties that have provided them a vast niche in the industry:

- High thermal and hydrothermal stability in the industrial environment, especially highly siliceous zeolites
- High internal surface area
- Presence of ion exchange ability allows the formation of highly dispersed catalytically active sites, such as highly acidic sites
- Pores structure provides shape selectivity (which has been shown to limit chain length growth to gasoline range hydrocarbons in methane conversion)
- High acidity promotes the oligomerisation, isomerisation, cracking and aromatisation reactions

The ZSM-5 type zeolite, which has all these properties, is the catalyst for this work due to its importance in the oligomerization processes.
Figure 1.11  Illustration of primary unit of TO$_4$ tetrahedral, 5-1 secondary building units, the MFI framework and channel structure of ZSM-5 zeolite (Klinowski and Barrie, 1988)
1.4.2 Magnesium Oxide-based Catalysts for OCM Reactions

Metal oxides act as important catalysts in the reaction of oxidative coupling of methane (OCM). The catalytic reaction of OCM over metal oxide surfaces has been intensively investigated over the past 20 years (Lintuluoto and Nakamura, 2004). There are still ongoing studies to find good catalysts to achieve more active and especially higher selectivity toward C₂ hydrocarbon (especially ethylene). Among the solids used in OCM as the main components or supports of numerous active and selective oxide catalysts, magnesium oxide occupies a special position. Catalysts based on MgO promoted with alkali oxides, alkaline earth oxides, rare earth oxides, etc., have been frequently used in the research.

It is widely accepted that the increase in surface basicity caused by a promoter enhances the activity and C₂ selectivity (the selectivity to C₂H₄ and C₂H₆) of MgO-based catalysts (Maitra, 1993). Only limited attention had been given to the activity of unpromoted MgO itself in the OCM process and to the role of MgO as a carrier in MgO-based catalysts. As noticed by some authors, the samples of MgO differing in origin and properties usually also varied in their catalytic performance. This phenomenon was usually related to the differences in morphology, the specific surface area, surface structure and properties, a type of precursor, the calcination time and temperature, etc. (Burrows et al., 1998; Lacombe et al., 1995; Kus et al., 2003; Kus et al., 2002b, Kus and Taniewski, 2002; and Maksimov et al., 1998).

Burrows et al. (1998) have pursued the structure sensitivity aspect of OCM catalyst design for MgO and doped MgO catalysts for a number of years. A perfect structure of MgO as a cubic (rocksalt) crystal is illustrated in Figure 1.12. However, under certain conditions or situations (such as addition of lithium), magnesium oxide has a highly defective surface structure showing steps, kinks, corners, and others which provide O²⁻ sites of low coordination. These low co-ordinated O²⁻ sites (O²⁻ on faces, O²⁻ on edges and O²⁻ on corners) are expected to be responsible for the strength of the basic sites (Pinarello, et al., 2001).
By comparing the microstructure and performance of pure MgO catalysts prepared by a number of very different routes, Burrows et al. (1998) have demonstrated that the selectivity and specific catalytic activity are unaffected by the number of corner or edge sites that the MgO exposes. That suggested that vacancies on the planar {100}-type surfaces of MgO are likely to be active sites for methane activation. They have also shown that the addition of lithium carbonate to MgO results in subtle changes in the surface structure. The improved catalytic performance of Li doped MgO was associated with, amongst other effects, the presence of dislocations creating active sites on the MgO surface.

The MgO properties/performance relationship still remains a controversial question. Although intensive investigations have been carried out, the nature of active sites formed in these oxides at high temperature are still a matter of debate. However, it is clear that the lattice defects of doped oxides play an important role in the reaction mechanism (Balint and Aika, 2001). This is not surprising since the lattice defects of a large number of oxide systems have been reported to play an important role in molecular activation at high temperatures. A part of the surface
oxygen becomes active at high temperatures, reacting with methane even on irreducible oxides such as MgO. The special oxygen structure such as O\(^{-}\), has been proposed as the active species. If O\(^{-}\) is the active species, O\(^{-}\) or the surface structure accepting O\(^{-}\) must be generated only at high temperature on MgO catalytic systems. Thus, it can be seen that the OCM reaction occurs on MgO only at high temperatures, usually 873–1073 K. Accordingly, Karasuda and Aika (1997) concluded that the OCM reaction occurs through such an activation step as is shown in Figure 1.13 when applying MgO based catalyst.

Figure 1.13  Model of oxygen atom flux in MgO-based catalysts where the fast exchange with an \(a\)-group O (O\(_a\)) in the MgO surface and the slow exchange with a \(b\)-group O (O\(_b\)) in MgO lattice (Karasuda and Aika, 1997)

Karasuda and Aika (1997) also focused their attention on MgO as a representative irreducible oxide for the OCM catalyst and have attempted to clarify the production mechanism of the active site. The authors have reported that the conductivity of MgO and Li/MgO is related to the defect structure produced by the decomposed impurity H\(_2\)O dissolved in the MgO lattice. The electric conduction is considered due to proton jumping at low temperatures, while hole conductivity prevails at high temperatures, where H\(_2\)O is dissolved in MgO (step 1 in Figure 1.14)
and the hole ($\text{O}^2- + \text{h}^+ = \text{O}^-$) is produced through $\text{H}_2$ evolution (step 2 in Figure 1.14). During the OCM reaction, $\text{O}^-$ (or hole + $\text{O}^2-$) reacts with methane to produce methyl radical and $\text{OH}^-$ (step 3 in Figure 1.14). Two methyl radicals combine to form ethane (and then ethene). The produced $\text{OH}^-$ is removed as $\text{H}_2\text{O}$ leaving the defect (step 4 in Figure 1.14) and dioxygen reproduces $\text{O}^-$ again (step 5 in Figure 1.14). If methane is not present but dioxygen is at the OCM temperature (step 5 in Figure 1.14), then the reverse reaction (step 6 in Figure 1.14) can be observed through the isotopic exchange. Thus, the isotopic exchange between dioxygen and MgO provides significant information on the active center of the OCM reaction.

\[
\begin{align*}
\text{O}^2- &\quad \text{Mg}^{2+} & \quad \text{O}^2- &\quad \text{Mg}^{2+} & \quad \text{Mg}^{2+} & \quad \text{O}^2- \\
\text{Mg}^{2+} &\quad \text{O}^2- &\quad \text{H} &\quad \text{H} &\quad \text{Mg}^{2+} &\quad \text{O}^2- \\
(1) &+\text{H}_2\text{O} &\quad -\text{H}_2 &\quad \text{O}^- &\quad \text{Mg}^{2+} &\quad \text{O}^- \\
(2) & &\quad \text{O}^- &\quad \text{Mg}^{2+} &\quad \text{O}^- \\
(3) &+2\text{CH}_4 &\quad \text{OH}^+ &\quad \text{HO}^- &\quad \text{Mg}^{2+} &\quad \text{O}^2- \\
(4) &-\text{H}_2\text{O} &\quad \text{O}^- &\quad \text{Mg}^{2+} &\quad \text{O}^- \\
(5) &+0.5\text{O}_2 &\quad -0.5\text{O}_2 &\quad \text{O}^2- &\quad \text{Mg}^{2+} &\quad \text{O}^2- \\
(6) & & & & &
\end{align*}
\]

**Figure 1.14**  Model of active center generation and the OCM reaction model
(Karasuda and Aika, 1997)

Currently, rare-earth-metal (REM) oxides, like La$_2$O$_3$, are among the most active catalysts for OCM, and a number of experimental studies centered around the mechanistic features of their chemistry have been reported. In the same way, Choudhary et al. (2000b) and Traykova et al. (1998) suggested that La-promoted MgO catalysts showed high activity and selectivity in the OCM process at a very high space velocity and also high catalyst stability in the process. The promotion effect of lanthanum was attributed to a large increase in the strong basicity of the catalyst because of the doping of MgO by lanthanum. Lacombe et al., (1994)
suggested that surface intermediates such as methoxide ions M-O-CH₃ are formed on the lanthanum oxide catalysts in the course of the OCM reaction. The formation of these species would be related to the dehydroxylation of terminal La-OH groups leading to the formation of a complex site \{O²⁻, vacancy\}; this site would allow the adsorption of a methyl radical colliding with the surface. Once stabilized, the La-O-CH₃ species would undergo a further oxidation. Thus, specific hydroxyl groups from the lanthana surface could act as methyl radical scavengers. Because of its high activity/selectivity and productivity (i.e. operation at high space velocity or low contact time), and also high thermal stability, the La-promoted MgO catalyst has a high potential for use in the OCM process.

1.4 The Statement of Problem

Efficient utilization of methane, the primary component of natural gas, is becoming an immediate goal as we face issues of diminishing natural resources. Unfortunately, the remote locations of most natural gas reserves make transportation of this fuel economically unreasonable. One means to exploit the remote gas sources is to first convert methane to more useful higher carbon products that can easily be transported to the consuming facility. However, existing methane conversion methods have proven to be prohibitively expensive. Thus, developing a less expensive catalytic conversion method is of great interest and technologically significant.

In particular, the direct catalytic conversion of methane into desired chemicals or liquid fuels is still a great challenge for the utilization of natural gas in the field of catalysis. The two approaches involved are direct conversion of methane with the assistance of oxidants and direct conversion of methane under nonoxidative conditions. For example, the heterogeneously catalyzed oxidative coupling of methane (OCM) seems to be one of the most promising routes to convert methane directly from the abundant natural gas into ethylene which is a feed-stock for chemical industry and/or by oligomerization of ethylene into transportation fuels. A wide variety of catalysts, mainly metal oxide based catalysts, have been studied and
reaction mechanisms have been proposed. Although significant progress has been achieved in the research and development of oxidative coupling of methane (OCM), it is still difficult to overcome the barriers of technical and economic problems. Two factors handicap commercialization of this process: (1) $C_2+$ selectivity and yield are too low and (2) technological novelty results in uncertainty for scale-up. Higher $C_2+$ selectivities and yields have to be achieved mainly by development of more selective catalysts, but optimization of reaction conditions, reactor design and operation also offers possibilities to improve catalytic performance.

The technological uncertainty is due to the fact that all results available until now have been achieved in laboratory-scale units, mainly in microcatalytic fixed-bed and small-scale fluidized-bed reactors. Due to the complexity of the OCM reaction scale-up can be associated with a loss in catalytic performance. Moreover, the severe reaction conditions, i.e. high temperature and exothermicity require new reactor designs. Therefore, experience from other selective oxidation reactions can be used only to a limited extent. Reactor development includes not only the choice of the reactor type but also the selection of materials and of the method of temperature control. Against this background, reaction engineering aspects of the OCM reaction play an important and crucial part in the attempt to make this process commercially viable.

In addition, one of the serious limitations of the OCM process is the low concentration of ethylene in the product stream. Separation of ethylene at a low concentration is not at all economical. One way to overcome this limitation of the OCM process is to convert the dilute ethylene present in the OCM product streams directly into much less volatile product streams, such as aromatics and/or gasoline range hydrocarbons, which can be easily separated. On the other hand, although OCM results in the production of hydrocarbons, this product is characterized by the lack of selectivity for a particular hydrocarbon type or carbon chain length. Hence, there is a great need for a highly active and selective ethylene transformation catalyst useful for converting ethylene at very low concentrations or partial pressures into liquid hydrocarbons. Consequently, a second catalyst becomes essential if selectivity for a particular product is required.
During the early days, H-ZSM-5 zeolite, which is one of the synthetic zeolite, was found to be a suitable catalyst for the conversion of methane to higher hydrocarbons. Later, ZSM-5 was modified to increase the conversion of methane and the selectivity of targeted hydrocarbons products. But, this catalytic process has not reached the commercializing stage and it needs development to obtain a more promising result. However, some earlier studies have demonstrated that acidic H-ZSM-5 zeolite catalyst has shown a reasonably good oligomerization performance for olefin products to higher hydrocarbons.

Taking advantages of both the exclusive functionality of OCM catalyst and good oligomerization activity of H-ZSM-5 catalyst, we propose here the dual catalyst bed concept. In the present study, we have applied these catalysts to a serial dual-bed system as an alternative methane conversion route to liquid hydrocarbons in the presence of oxygen. The development of a combination of an OCM catalysts and H-ZSM-5 would overcome the inherent limitations and permit the direct conversion of methane to liquid hydrocarbons via a single reactor process. Therefore, a reactor system with such a function would be the focus of in this research.

1.5 Hypothesis

Taking advantages of both the exclusive functionality of OCM catalyst and good oligomerization activity of H-ZSM-5 catalyst, we propose here the dual catalyst bed concept. In the present study, we have applied these catalysts to a serial dual-bed system as an alternative methane conversion route to liquid hydrocarbons in the presence of oxygen. The development of a combination of an OCM catalysts and H-ZSM-5 would overcome the inherent limitations and permit the direct conversion of methane to liquid hydrocarbons via a single step reactor process. Therefore, a reactor system with such a function would be the focus of in this research.

The first catalyst comprises rare earth and alkaline earth metal oxides that are good materials for producing good-performance OCM catalysts and methane
conversion. Rare earth oxides have been thought to be good catalysts for the OCM reaction, and alkaline earth oxides have been found to be good promoting materials for rare earth oxides. Therefore, the first catalyst is preferably lanthanum promoted MgO catalyst that is believed to give better C₂ selectivity. The second catalyst comprises an intermediate pore size zeolite, HZSM-5 which further provides shape selectivity (which has been shown to limit chain length growth to gasoline range hydrocarbons) and its high acidity is effective to promote the oligomerization, isomerization and aromatization reactions involved in the restructuring of the primary OCM products. Apart from that, recent research showed that that metal loaded HZSM-5 catalysts are suggested to be potential catalysts for direct conversion of methane to liquid hydrocarbons. Therefore, metal-containing HZSM-5 catalysts can produce C₅⁺ liquids from OCM intermediate products if dehydrogenation and oligomerization functions of the metal are in balance. Hence, performance of the HZSM-5 catalysts with combination metals of (Ni, Mo and Cu) is tested through this research.

Furthermore, the process of this study is directed to converting high percentages of the methane present in mixed methane-oxygen containing feeds to OCM products at the first stage, while simultaneously converting mainly olefins to gasoline range liquid hydrocarbons at the second stage. In this way, the complexity of the separation processes needed in the ethylene recovery process also could be minimized.

1.6 Research Objectives

The main objectives of this research are:

i) To develop a lab scale dual-bed catalytic reactor system that is capable of catalyzing the production of liquid hydrocarbons from methane

ii) To elucidate the effect of reaction parameter on the dual-bed system
iii) To modify H-ZSM-5 with different kinds of metal and investigate the performance of this modified H-ZSM-5 catalysts on the products distribution as a function of types of metal.

iv) To find the optimum operating conditions required for maximum catalyst activity

1.7 Scope and Structure of this Thesis

This thesis focuses on the experimental study of a dual bed catalytic system over La-MgO and H-ZSM-5 based catalysts in accordance with the purposes of the present invention as embodied and broadly described herein, to produce liquid hydrocarbons from the methane gases. Thus, in this work, the possibility of liquid hydrocarbon production by means of the dual-bed system was investigated, and the effects of some reaction conditions were also explored. The focus is also given on the modification of the second bed catalyst of H-ZSM-5 by introducing some metal via incipient impregnation method in order to improve the yield of targeted products. Furthermore, it also involved the characterization of some catalysts in order to determine catalyst behavior. In addition, we report for the sequential optimization strategy for liquid hydrocarbons production through statistically designed experiments as an effective tool for medium engineering.

The thesis is divided into six chapters. Basically, an introduction with a short overview of the literature data on the particular topic is given in each chapter. In Chapter 1 the literature review which is related to the subject of this thesis has been reviewed briefly. The background regarding the properties of the zeolites and OCM catalysts are included in Chapter 1 as well as some theory on aspects of this research. The relevance of heterogeneous catalysis and the necessity to understand catalytic processes on microscopic scale are also accentuated. Furthermore, the fundamental concepts of catalytic conversion of methane is offered in this chapter. In addition, the applicability of our experimental approach to solve problems in applied catalysis is discussed. The objective of the research has also been elaborated in this section.
Chapter 2 outlines the experimental apparatus used and the experimental procedures. This chapter provides a brief description of the catalyst preparation procedures using conventional impregnation method. Moreover, the additional sections of this chapter focus on the general experimental procedures used throughout this work and the analytical techniques employed to interpret catalytic activity of all the catalysts. This chapter also describes the basic concept and the detailed procedures of the characterization method employed in this study.

Chapter 3 deals with the structural characterization and study the influence of the acidic behavior of the H-ZSM-5 catalyst in explaining the catalytic reaction performance of the dual bed system. Moreover, the influence of temperature and the effect of oxygen concentration on the activity and products selectivity as well as the result of the use of different SiO₂/Al₂O₃ ratio zeolite matrix were studied. A systematic approach is undertaken to study the influence of SiO₂/Al₂O₃ ratio and thermal treatment on the acidity and its nature, and the implication thereof for the intermediate OCM products conversion. The catalysts are characterized by TPD-ammonia techniques and the observed differences are correlated with the structural properties of the respective materials and catalytic activity.

Chapter 4 deals with the same system as Chapter 3 but focuses mainly on the role of metallic sites in order to obtain relations between the structural properties and the catalytic activity of the modified H-ZSM-5 catalysts in the conversion of methane through the dual bed strategy. The experimental phase was carried out in a dual-bed reactor in order to screen the catalysts and to identify the best one among the eleven metal-based H-ZSM-5 catalysts. The screening tests were conducted at fixed temperature of 700°C and CH₄/O₂ ratio of 10. In this chapter, some of the important matter are addressed in explaining the advanced performance of metal based H-ZSM-5 catalysts in this dual bed system, compared with unloaded H-ZSM-5 when applied as second bed catalysts, under fixed other reaction parameters. Moreover, the simplified reaction scheme to describe the reaction path in this dual bed system proposed by employing the recent products spectra in light of the previous literature is also reported.
Chapter 5 describes a study to develop an approach that would enable us to better understand the relationships between the variables (temperature, oxygen concentration and amount of Ni loading (wt%) and the response (yield of C\textsubscript{5+} hydrocarbons); and to obtain the optimum conditions for liquid hydrocarbons production using central composite design (CCD) and response surface methodology (RSM). The CCD has the advantage to predict responses based on a few sets of experimental data in which all factors are varied within a chosen range. The range of each variables was chosen based on the finding from one-factor at a time techniques. An empirical model including the effects of independent variables has also been developed through utilized software to represent the response surface. Also, TPD ammonia and NA characterization analysis were performed on the Ni loaded H-ZSM-5 catalysts to explicate the effect of modification of Ni on the catalytic reaction through the proposed system.

Finally, the results and findings of this thesis are summarized in Chapter 6. The future work possibilities are also suggested in this chapter.


Xing, E., Mi, Z., Xin, C., Wang, L. and Zhang, X. (2005). Endo- to Exo- Isomerization of Tetrahydrodicyclopentadiena Catalyzed by Commercially


